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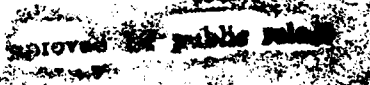
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# Investigation of Dipolar Reorientation Dynamics of Pure Bulk Polymers Using Second Harmonic Generation

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## Abstract

Second harmonic generation (SHG) in three corona-poled, pure, bulk polymers is studied as a function of temperature. It is found that this technique readily yields dynamical information that is complementary to that obtained from the technique of dielectric relaxation (DR). The SHG results are compared to those from DR in the same temperature ranges above  $T_g$ . It is found that in the temperature ranges examined, the relaxation times obtained from SHG are several orders of magnitude longer than those measured by dielectric relaxation. This is explained as being due to the strong correlation between oriented dipoles and to trapped charges injected by the poling process. Fitting measured data to the Williams-Landau-Ferry (WLF) equation indicates that more free volume is needed in SHG for dipolar reorientation than is needed in DR. An SHG relaxation elongation phenomenon at constant temperature is found to occur in the pure bulk polymers and is similar to that found in chromophore-doped polymers previously studied. The SHG technique is developed as a new tool to directly study the reorientational dynamics of polar polymer segments.

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## Introduction

Investigations into different aspects of molecular motion in bulk polymers will provide insights into the relaxation of macroscopic properties of polymeric materials. One type of molecular motion that is of interest is the reorientation of segments in a polymer chain. The segmental reorientational motion of a polymer chain is closely connected to local intra- and inter-segmental interactions and thus probing the dynamics of segmental reorientation could reveal much information about molecular motion in polymers in the liquid and solid states.

A commonly used technique to investigate the dynamics of segmental reorientation is dielectric relaxation (DR) which involves studying the linear response of the molecular system as an external AC electric field is applied to it. In the DR technique one measures the real and imaginary parts of the dielectric constant at the frequency of the applied AC field. The measured quantities are interpreted in terms of the dynamics of orientation fluctuations from equilibrium of segmental dipole moments in the polymer chain.<sup>1</sup>

Second harmonic generation (SHG) has recently been applied as an additional technique for investigating segmental reorientation dynamics.<sup>2,3,4,5,6,7</sup> SHG is concerned with exposing the material to a light beam at frequency  $\omega$  and observing the response at  $2\omega$ . The current practice when attempting to study polymeric molecular motion using SHG is to "label" the polymers by either doping, or covalently attaching, hyperpolarizable molecular chromophores to the polymer chains.<sup>8</sup> In this case, the SHG signal of the nonlinear optical (NLO) polymer arises mainly from the dipolar orientation of the chromophores whose orientational states are influenced by the polymer environment; thus, the temporal behavior of the SHG signal contains

information about the motional dynamics of the host polymer. However, the technique, as such, is indirect since information extracted about polymer segmental motion comes from chromophore reorientation rather than directly from the polymer.

Since the SHG response is derived from a second order optical susceptibility, it vanishes identically in an isotropic amorphous polymer system. Therefore, to observe SHG, the isotropic symmetry of the amorphous system must be broken and a polar orientational order induced in the medium. This is commonly accomplished by the process of electric field poling.

<sup>8,9</sup> Since any molecular moiety (such as a polar segment in a polymer chain) lacking inversion symmetry must also have a nonvanishing first order hyperpolarizability, it should be possible to observe an SHG response from an unmodified blank polymer containing polar groups provided that the centrosymmetry in the medium can be removed. The temporal dependence of the SHG signal induced after the poling field is removed would thus contain information about the dynamics of reorientation of the previously aligned polar segments. As a result, like DR, the SHG response from the blank bulk polymer would provide direct information about segmental reorientation dynamics.

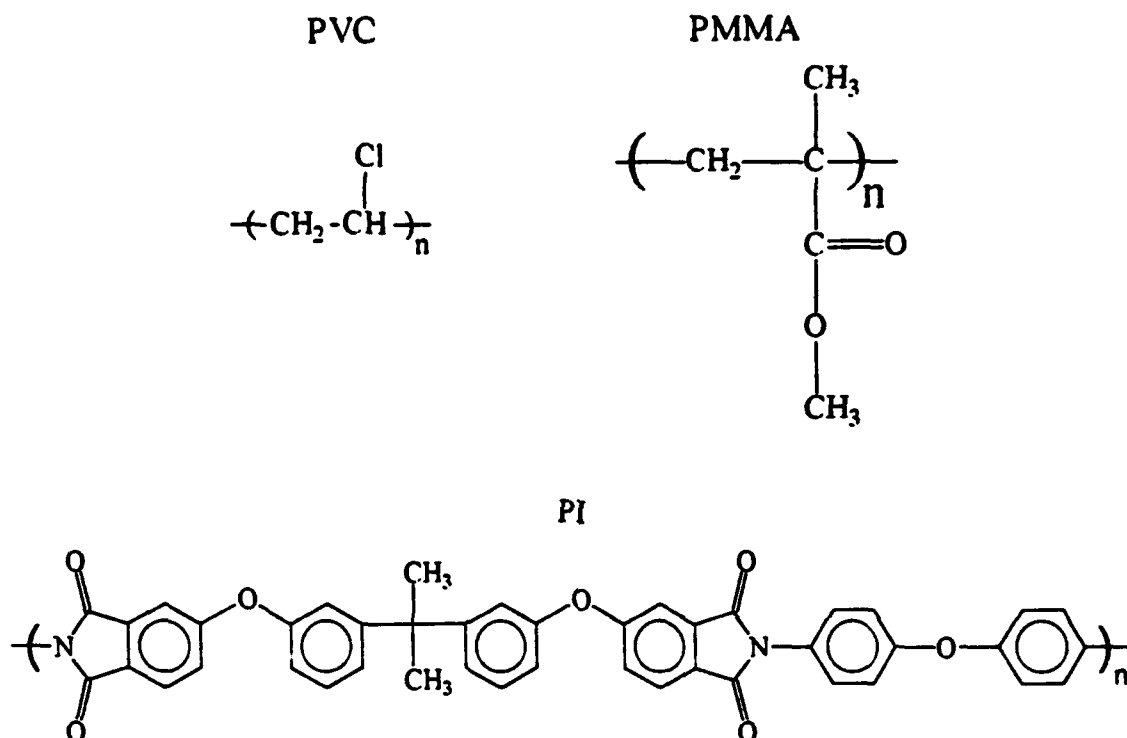
Although the information that can be obtained from the two techniques is similar in nature, there are differences between DR and SHG. In DR one is concerned with the dynamics of fluctuations of polar segments in a system *at equilibrium*. On the other hand, due to the application of a strong polarizing electric field in the SHG method, the polymer sample is *not in a state of equilibrium* upon removal of the applied field; the decay of the SHG signal then reflects the reorientational dynamics of those polymer segments that had been oriented by the field.

Another important difference between SHG and DR is that whereas DR involves only the ground state dipole moment of the polar groups, SHG is affected not only by the ground state dipole moment but also by the transition dipole moments and the excited state dipole moments. In the case of the SHG induced by the NLO chromophore in labeled systems, the contribution of the intramolecular charge transfer band is dominant. The molecular structure of the intramolecular charge transfer NLO chromophores is generally rigid: the transition moment dipole and excited state dipole moments are in general parallel to the ground state dipole moment. Thus, one expects that in the low field poling condition (i.e. when the dipole-electric field interaction energy is less than thermal energy) information regarding dipolar reorientational dynamics obtained from SHG to be the same as that obtained from DR, as under this condition both SHG and DR are associated with the same time correlation function.<sup>10</sup> On the other hand, SHG in the blank polymer is not enhanced by the intramolecular charge transfer state and, in addition, it is not known that the transition dipole moments involved in SHG are rigidly parallel to the ground state dipole moment of the polar group. Thus, one would not expect the DR and SHG techniques to yield the same dipolar reorientational dynamics in blank polymers.

In this paper, we report results of SHG studies on unmodified pure polymers and demonstrate for the first time that SHG can be used to probe the segmental movement of polymer chains in a blank polymer and thereby obtain quantitative information about chain reorientation dynamics in the bulk polymer. We also show that information obtained from SHG is not identical, but rather complimentary, to that from DR.

## Experiment

To demonstrate the technique, we used polymethylmethacrylate (PMMA) (Aldrich, 18226-5,  $M_w = 506,000$ ), polyvinylchloride (PVC) (Aldrich, 18956-1, high molecular weight) and polyimide (PI) (Shanghai Institute of Synthetic Resins, YS-30, unmeasured molecular weight). The structures of these three polymers are



To assure purity, all polymers were washed before use: the polymers were first dissolved in chloroform ( $\text{CHCl}_3$ ) and then precipitated by gradually adding methanol. The resulting powdered polymers were collected and dried in a vacuum oven at an elevated temperature ( $65^\circ\text{C}$ ; above the boiling point of chloroform and ethanol) to remove solvent. (The absence of solvent is checked using infrared absorption spectroscopy and thermogravimetric analysis) This process was repeated three times for each polymer before use. The  $T_g$ 's of the polymers were determined by differential scanning

calorimetry (DSC, Perkin-Elmer Delta Series, scanning rate 20 °C/min) and were 119 °C, 79 °C and 207 °C for PMMA, PVC and PI, respectively. (As measured, our  $T_g$ 's for PMMA and PVC compare favorably with those reported elsewhere in the literature;<sup>11</sup> a literature value for the  $T_g$  of our particular PI was not available at the time of writing) The setup for SHG measurement (the excitation source was a Q-switched Nd:YAG laser operating at 10 Hz with a fundamental beam of 1064 nm; the detection system consisted of a photomultiplier tube connected to a boxcar integrator) and the method in which thin films were made (spin coating) have been described in previous work.<sup>12</sup> To achieve high poling fields all polymer films were polarized (poled) by the corona discharge technique which has been thoroughly described in the literature.<sup>8,9,13</sup> During the poling/SHG signal relaxation experiments the sample was kept under isothermal conditions in a specially-designed oven, equipped with optic windows, the temperature of which could be maintained to within  $\pm 0.1$  °C with a temperature controller (Omega CN2042).

## Results and Discussion

Shown in Figure 1 are two growth/decay curves of the SHG signal of PI, obtained *in situ* at 207 °C (i.e. poled at 207 °C with the signal growth and decay also observed at 207 °C; note that 207 °C is near the  $T_g$  of PI). The sample was poled with a corona discharge using a positive voltage of 2.5 kV applied to the tip of a tungsten needle placed 1 cm away from the polymer film. When the sample was first poled, the SHG signal grew rapidly and then assumed a less gradual growth to a constant plateau value; it took about 7.5 minutes to reach a plateau signal. (All subsequent experiments used a poling of this duration) Upon turning off the

corona discharge voltage, the SHG signal decayed to zero (i.e. there was no SHG signal above instrumentation background; this was also true before any poling on the sample had been done) in about 25 min (1500s). After the signal had decayed, we again turned on the 2.5 kV discharge voltage. This time we observed a nearly instantaneous rise and then a rapid establishment of the plateau signal, instead of a two-steps growth/plateau pattern as found during the initial poling stage (Figure 1).<sup>14</sup> The magnitude of the second plateau is about 10% less than the magnitude of that obtained initially.<sup>15</sup> When the discharge voltage was turned off after the poling duration, the SHG signal took a longer time than previously to decay to its background value. As the poling/decay process was subsequently repeated, a successively longer decay was found until a steady state decay time of over 2000s was reached. After this steady state decay curve was reached, there was no longer any change in the decay time constant, regardless of the number of times that the sample was subsequently poled. Changing the sample temperature led to a different steady state decay time but the pattern was the same. The lengthening of the SHG decay curve is clearly demonstrated in Figure 2, which shows two SHG decay curves for PI, with the first curve obtained after the initial poling and the second one obtained after the steady state was reached. Similar poling and SHG signal decay behavior was also observed in the PMMA and PVC samples.

We have recently reported a similar SHG instantaneous rise followed by a decay elongation phenomenon in NLO chromophore doped guest/host polymer systems subject to successive poling/decay cycles.<sup>16,17</sup> In these experiments, the contact electrode poling technique was used. We have attributed the instantaneous growth of the SHG to the elastic stress induced by the poling field as well as the field arising from injected charges (electrons) which are trapped in the polymer upon termination of poling. The lengthening of the SHG



decay was explained as due to the gradual accumulation of injected electronic charges which assist the correlation and stabilization of the aligned chromophore dipoles. In the absence of the injected electronic charges, the dipolar alignment in the shoulder-to-shoulder configuration is energetically unfavorable. However, the parallel shoulder-to-shoulder dipolar alignment becomes stable in the presence of injected charges. In other words, charge injection assists in partially aligning the segmental dipoles.

Recently Wang, Jarnagin and Samulski (WJS) also reported a two-step rise in a corona poled NLO side-chain polymer.<sup>18</sup> They interpreted their observation as due to a rapid orientation of side chain NLO chromophores, followed by a slow polymer chain contour rearrangement. However, the PI chain does not have a readily orientable side chain and it is thus difficult to use their proposed model to account for the two-step SHG growth pattern observed during the initial poling of the blank PI, despite the fact that the WJS model does not contradict the two step SHG growth signal which we also observed in PMMA and PVC, both of which have orientable polar side groups. It is also difficult to apply the WJS model to account for the nearly instantaneous rise of the SHG signal observed in each blank polymer after the initial poling/decay cycle.

The SHG signal,  $I_{SHG}$ , decay curves of the blank polymers studied are not single exponential. However, we were able to successfully fit the curves to a stretched exponential or Kohlrausch-William-Watts (KWW) form given by<sup>19</sup>

$$\chi^{(2)} \propto \sqrt{I_{SHG}} = ae^{-(t/\tau)^\beta} \quad (1)$$

where the width parameter  $\beta$  ( $0 < \beta \leq 1$ ) and the characteristic relaxation time  $\tau$  are different

in different polymers. Since the SHG intensity is proportional to  $|\chi^{(2)}|^2$ , where  $\chi^{(2)}$  is

the second order nonlinear susceptibility, we take  $\sqrt{I_{SHG}}$  to fit the time dependence of the second order susceptibility. In Table I, we report  $\beta$  and  $\tau$  values for the three polymers studied at temperatures above  $T_g$ . Experimentally, we have found that above  $T_g$ , the  $\beta$  parameter of these blank polymers increases with increasing temperature whereas the characteristic relaxation times,  $\tau$ , varies inversely.

Two types of functions have been used to fit the relaxation data for both the sidechain and the chromophore-doped NLO polymers. In the case of the guest/host NLO polymer which was poled by contact electrodes, upon turning off the poling field, followed by immediate grounding of the electrodes (which bleeds out the accumulated surface charges), we showed previously that the decay of the SHG signal obtained in this way could be satisfactorily fit to a single exponential.<sup>10</sup> However, if the NLO polymer is poled with the corona discharge method (regardless of whether it is of the guest/host, side- or main-chain variety), a much better fit of the SHG decay was made to a single Kohrausch-Williams-Watts (KWW) function as given by Equation (1).<sup>5,12</sup> The difference found in the SHG decay behavior between a sample that has been corona-poled and one that has been contact-poled is interpreted as due to the presence of surface charges in the corona discharge poled films which cannot be easily bled off in the *in situ* experiment without significantly disturbing the charge deposition or temperature uniformity of the sample. The presence of surface charges will prolong the SHG signal decay. To use the contact electrode poling technique to achieve the high poling fields needed in the present experiment, stringent requirements on film quality are needed to eliminate pinholes; the presence of a single pinhole will lead to an electric breakdown at even moderately applied voltages. Thus, although contact poling would have eliminated some of the complexities (mentioned above) associated with corona poling, we were not able to obtain high

enough fields in our samples with the contact poling method to allow the observation of SHG in these polymers. Thus, due to the fact that the surface charges accumulated in the corona poled films cannot easily be bled out in our sample assembly, in order to interpret the SHG signal decay, factors concerning surface and injected charges must be taken into account when describing the orientational dynamics of the corona poled blank polymer.

We have observed an elongation effect of the SHG decay time of the medium subject to repetitive poling/decay cycles. The results from such a study done on a PI sample at 207 °C are shown in Figure 3 where the ratio of relaxation time is plotted as a function of elapsed time,  $t_{elp}$ . The elapsed time,  $t_{elp}$  is not identical to the aging time of the sample. The physical aging process plays a role in affecting the relaxation time below  $T_g$  because in the vernacular of free volume theory, the amount of free volume available for reorientation of the dipolar segments decreases with time as the sample is aged below  $T_g$ . The decrease in free volume reduces the reorientational mobility, which in turn lengthens the relaxation time. In the physical aging experiments, the relaxation time is related to the physical aging time by a power law,  $\tau = At_a^\gamma$ ,<sup>20</sup> where  $t_a$  is the aging time and  $\gamma$  is a quantity between 0 and 1. Near  $T_g$ ,  $\gamma$  is less than 1 and is 1 below  $T_g$  for strong aging. Physical aging may play a role in the lengthening of the relaxation at 207 °C for PI (around  $T_g$ ). In Figure 3, we plot the relaxation time  $\tau$  versus  $t_{elp}$  and obtain  $\gamma = 0.3$  at  $T = 207$  °C which is near the glass transition temperature of PI. However, due to the fact that the relaxation time elongation is also observed in the sample above  $T_g$ , the gradual accumulation of injected charges in the medium following each poling/decay cycle (mentioned above) is believed to be a more important mechanism contributing to the lengthening of  $\tau$ .

After fitting SHG decay curves to Equation (1), the average relaxation time  $\langle \tau \rangle$  can be calculated according to<sup>21</sup>

$$\langle \tau \rangle = \frac{\tau \cdot \Gamma\left(\frac{1}{\beta}\right)}{\beta} \quad (2)$$

where  $\Gamma(x)$  is the gamma function (Table I). The calculated average relaxation times given in Table I for PI, PMMA and PVC are plotted versus  $1/T$ , where  $T$  is the absolute temperature, in Figure 4. It must be emphasized that due to the relaxation elongation effect mentioned above, if the sample is not subjected to a sufficient number of poling/decay cycles, reproducible results cannot be realized. The values given in Table I and Figure 4 were extracted once a steady state decay curve was obtained. It should be noted that above  $T_g$  the average relaxation time  $\langle \tau \rangle$  varies smoothly with temperature. The temperature dependence is, however, not Arrhenius. Below  $T_g$ , the  $\langle \tau \rangle$  data show a much weaker temperature dependence as indicated by the PVC result.

Figure 5 contrasts the difference between average relaxation times obtained from our SHG experiments and those obtained from the dielectric relaxation technique for PVC<sup>1,22</sup> at various temperatures. The average relaxation times for dielectric relaxation were calculated by assuming that  $\langle \tau \rangle = f_{\max}^{-1}$ , where  $f_{\max}$  is the frequency at maximum  $\epsilon''$  (the imaginary part of the dielectric constant). Two observations regarding this figure are important to point out: first, as mentioned above, relaxation times obtained from  $I_{\text{SHG}}$  decay for PVC below  $T_g$  show a weak temperature dependence and, in fact, do not follow the Williams-Landau-Ferry (WLF) equation<sup>23</sup> obtained above  $T_g$ . At temperatures below

$T_g$ , the polymer is in the glassy state, main chain motions occur only on the very slow time scale associated with slow volume relaxation and the chain dipole reorientation is due probably to the  $\beta$ -motion; as such, the SHG relaxation time is not expected to change with changing temperature in the same manner as that above  $T_g$  when main-chain  $\alpha$ -motion takes place. Second, and most important, the SHG relaxation is several orders of magnitude slower than the dielectric relaxation. The relaxation time difference is much larger at high temperature (about  $10^4$  times larger at 110 °C) and becomes smaller as  $T_g$  is approached from above. At  $T_g$  the two relaxation times are nearly equal. The large difference between the two results above  $T_g$  is, of course, associated with the much higher electric field that is used to polarize the sample and the presence in the sample of injected charges that help to correlate the dipoles. The KWW function given in Equation (1) to describe  $\chi^{(2)}$  gives an account of the distribution of relaxation times of the orientational correlation function associated with the SHG signal decay. In the present case, the SHG signal decay is due to reorientation of polymer segmental dipoles that are strongly correlated. The quantity  $\langle \tau \rangle$ , given in Equation (2), describes the average relaxation time of the dipoles that lose the orientational correlation. One notes that the change in the temperature dependence of  $\langle \tau \rangle$  versus  $T^{-1}$  above and below  $T_g$  in the present case differs from the temperature dependence of NLO polymer guest-host systems previously reported in which no abrupt difference in the temperature dependence is detected in the vicinity of  $T_g$ . The difference is believed to be associated with the plasticizing effect of the NLO chromophores<sup>24</sup> which are, of course, absent in the present blank polymer systems.

Using different polarizations of the incident laser beam, one can separate from the SHG experiment two second order optical susceptibilities,  $\chi_{31}^{(2)}$  and  $\chi_{33}^{(2)}$ . The decay of  $\chi_{31}^{(2)}$  and  $\chi_{33}^{(2)}$  are due to the relaxation of polar order parameters,  $L_{31}$  and  $L_{33}$ , which are given by

$$\begin{aligned} L_{31}(t) &= \frac{1}{2} \left[ \langle \cos \theta(t) \rangle - \langle \cos^3 \theta(t) \rangle \right] \\ &= \frac{1}{2} \left[ \langle P_1(\cos \theta(t)) \rangle - \langle P_3(\cos \theta(t)) \rangle \right] \end{aligned} \quad (3)$$

$$\begin{aligned} L_{33}(t) &= \langle \cos^3 \theta(t) \rangle \\ &= \frac{1}{5} \left[ 3 \langle P_1(\cos \theta(t)) \rangle + 2 \langle P_3(\cos \theta(t)) \rangle \right] \end{aligned} \quad (4)$$

where  $\theta$  is the polar angle of the axis of the dominant component of the hyperpolarizability tensor of a representative segment and  $P_n$  is the Legendre polynomial of order  $n$ . As an approximation, the dominant hyperpolarizability element is assumed to be along the direction of the dipole moment of the polar segment. Since segment dipoles reorient, angle  $\theta$  is a function of time.

The plateau SHG intensity is proportional to the square of the initial value of the order parameter of the polar orientation. If the incident radiation is p-polarized (the E-field in the plane of incidence), the plateau intensity is proportional to a combination of  $L_{33}^2(t=0)$  and  $L_{31}^2(t=0)$ ; on the other hand it is proportional to  $L_{31}^2(t=0)$  if s-polarized incident radiation (the E-field perpendicular to the plane of incidence) is used to excite the SHG signal (here  $t=0$  sets the origin of the time at the end of the poling duration). Several versions of the oriented gas model have previously been used to calculate the initial value of the order parameters.<sup>7,25</sup> Recently, the Meier-Saupe mean-field model<sup>26</sup> as well as a non-mean field statistical mechanical

calculation<sup>27</sup> have also been employed to calculate the order parameters at  $t = 0$ . It can be shown from these models that if the poling field-dipole interaction energy,  $pE$ , is less than the thermal energy  $kT$ , then one obtains  $L_{33}^2(t=0) = 3L_{31}^2(t=0)$ . In other words, for the condition that the poling parameter  $a \left( = \frac{pE}{kT} \right) \ll 1$ , the term  $\langle P_3(\cos\theta) \rangle$  is not excited. This result is quite general and does not depend on the type of the intermolecular interactions which are present in affecting the segmental alignment.<sup>27</sup>

Thus, one can infer from above, that in the weak poling field condition, the information concerning the reorientational dynamics that one obtains from the SHG relaxation study would be similar to that derived from the DR technique, for the reason that in DR one is also concerned with the decay of the quantity  $\langle P_1(\cos\theta(t)) \rangle$ .<sup>1</sup> The Debye-type small angle rotational diffusion model has been inferred to describe the relaxation of the polar orientational order parameters  $\langle P_j \rangle$  (and also  $\langle P_3 \rangle$  in the high poling field case).<sup>28</sup> However, the Debye type model deals only with reorientation of an uncorrelated dipole; the correlated reorientational motion of dipoles, which is very important in describing the SHG signal is not treated in the Debye diffusion model. Thus, we believe that the Debye diffusion model is inadequate for the description of the SHG signal growth or decay.

The effect of correlated reorientational motion on the SHG signal decay has been considered by Wang *et al.*<sup>10,12,16,17</sup> In general, the relaxation time  $\tau$  associated with the orientational parameter in SHG is given by<sup>10</sup>

$$\tau = \frac{\chi^{(2)}}{\mu} \quad (5)$$

where  $\tau$  is the SHG signal relaxation time,  $\chi^{(2)}$  is the second order susceptibility and  $\mu$  is the rotational mobility. Due to the imposition of a strong poling field,  $\chi^{(2)}$  in the SHG experiment depends strongly on the poling field: under low poling fields both  $\chi_{33}^{(2)}$  and  $\chi_{31}^{(2)}$  increase linearly with increasing poling field strength whereas under high poling fields  $\chi_{33}^{(2)}$  increases and  $\chi_{31}^{(2)}$  decreases with increasing poling field strength. If  $\chi_{31}^{(2)}$  increases with increasing poling field, then in accordance with Equation (5), the SHG signal relaxation time is expected to increase with increasing poling field strength provided that the mobility  $\mu$  is not affected by the poling field. This effect has been demonstrated in an NLO polymer.<sup>10,16</sup> The increase in  $\tau$  may also be enhanced considering the fact that injected electronic charges are expected to strongly correlate segmental dipoles, thereby further retarding the decay of the polar order parameter.

Both dielectric relaxation and SHG are sensitive to orientational pair correlation (OPC) effects. Whereas the OPC effect in dielectric relaxation is associated with dipolar orientational fluctuations in the system at equilibrium, the OPC effect in SHG is associated with the relaxation of oriented dipoles in the non-equilibrium system due to the imposition of the strong electric field. The electric field aligns the dipoles and enhances the orientational pair correlation effect. However, as mentioned above, if the poling field/dipole interaction is small compared with  $kT$  and if the polymer dielectric property is not changed by the injection of charges from poling, then in accordance with linear-response theory, one would expect the SHG relaxation time to be identical to that for dielectric relaxation.<sup>10</sup>



However, the decay of the SHG signal can be hindered by the strong correlation between dipoles due to the applied corona field and by charges injected into the polymer which further correlates the segmental dipoles. In a similar manner, the mobility  $\mu$  may also be affected by the poling field or the trapped charges. According to Equation (5), the relaxation time  $\tau$  would decrease with increasing the poling field if the poling field exerts a greater effect on the mobility than on the susceptibility. In fact, the situation in which the SHG relaxation time decreases with increasing poling field has also been observed in a guest/host NLO polymer in which the polymer host is known to have a great affinity for electrons.<sup>12</sup>

From the above discussion, we have shown that the relaxation time above  $T_g$  associated with the SHG signal decay is expected to be much longer than that obtained from using DR. These conclusions are borne out in the present study.

In Figures 4 and 5, the solid curves are fits according to the Williams-Landau-Ferry (WLF) equation<sup>23</sup>

$$\log\langle\tau\rangle = \log(\tau_\infty) + \frac{C_1 C_2}{T - T_g + C_2} \quad (6)$$

where  $\tau_\infty$  is the relaxation time at very high temperature and  $C_1$  and  $C_2$  are the WLF constants appropriate for SHG. Fits to our SHG data yielded values of  $8.1 \times 10^{-2} s$ , 3.7 and 50 K for PVC,  $4 \times 10^{-4} s$ , 6.5, and 80 K for PMMA and 9.8s, 2.5 and 27.5 K for PI for  $\tau_\infty$ ,  $C_1$  and  $C_2$  respectively. These SHG values for PMMA and PVC should be contrasted with the dielectric results of  $2.0 \times 10^{-14} s$ , 12.5 and 80 K for PMMA<sup>29</sup> and  $2.3 \times 10^{-16} s$ , 19.4 and 48.4 K for PVC<sup>30</sup>. One notes that the values for  $C_2$  differ for PVC and PMMA and that the  $C_2$  values obtained from SHG are rather similar to those obtained

from dielectric relaxation spectroscopy. Also, the  $C_1$  values obtained from SHG are smaller than those from dielectric relaxation and the  $\tau_\infty$  values for SHG are much larger than those from DR. These results reflect the fact that the relaxation times obtained from SHG are considerably longer than those obtained from dielectric relaxation.

As is well known in free volume theory,<sup>1,23</sup> the average relaxation time  $\tau$  is related to the fractional free volume  $f$  by  $\tau = \tau_\infty \exp\left(\frac{B}{f}\right)$ , where the parameter  $B$  depends on the physical process involved. (e.g. the  $B$  parameter for viscosity is larger than that for probe diffusion involved in holographic grating relaxation experiments<sup>31</sup>) A process associated with a greater correlation effect will be associated with a smaller  $B$  parameter. The WLF coefficient  $C_1$  is related to  $B$  by  $\frac{B}{f_g}$  and hence  $C_1$  is technique dependent, whereas the

WLF coefficient  $C_2$  is universal as it is determined by  $\frac{f_g}{\alpha_g}$ . Here  $f_g$  and  $\alpha_g$  are the

fractional free volume and the thermal expansion of the polymer at  $T_g$ , respectively. If we assume that the fractional free volume at  $T_g$  is constant,<sup>23</sup> then a small  $C_1$  value indicates that considerably more orientational correlation is involved in SHG than is involved in DR.

Thus, as mentioned above, at high temperatures  $\langle \tau \rangle$  obtained from our corona-poled SHG experiment is much longer than that from DR but, at temperatures near or below  $T_g$ , the relaxations observed in DR and SHG occur on approximately the same time scales. These observations agree with the results presented in reference 2 but are not in agreement with those of Dhinojwala, *et al.*<sup>32</sup> and Eich *et al.*<sup>3</sup> who both used the contact-poling technique in their experiments. These large differences are likely associated with

the enhanced correlation among oriented dipoles in the presence of injected charges in the SHG experiments using corona poling. Above  $T_g$  polymer chains rapidly undergo reorientation and the injected charges play an important role in correlating the dipoles and slow down the dipolar fluctuations. Near  $T_g$  chain motion has slowed down considerably and the effect of injected charges on the dipolar reorientational process is not expected to be as strong in comparison with that above  $T_g$ . As a result, the average relaxation times obtained for the SHG and DR techniques because nearly equal as  $T_g$  is transversed from above.

## Summary and Conclusion

In conclusion, we have shown for the first time that SHG can be used to study the dynamics of polar segment reorientation in pure bulk polymers that have been poled using the corona discharge technique. We have demonstrated that this technique can yield information complementary to that obtainable through dielectric relaxation although it must be kept in mind that while DR is a technique monitoring dipolar fluctuations from equilibrium, SHG signal decay measures the dynamics of a system that is not in equilibrium. We have determined that the Kohlrausch-William-Watts function provides a good fit to the SHG signal relaxation curves. Data from temperature dependence measurements has illustrated that at temperatures above  $T_g$ , the SHG relaxation time is several orders of magnitude longer than DR relaxation; this has been interpreted as due to enhanced dipolar correlation between dipoles due to the presence of trapped charges. As the temperature approaches  $T_g$  from above we have found that the relaxation observed in DR and SHG occur on approximately the same time scale. This is attributed to the gradual slowing down of the chain motion which mitigates the charge-enhanced dipolar orientation effect. Above  $T_g$ , the WLF equation gives a satisfactory fit to temperature

dependence relaxation data for the three polymer systems examined in this paper. Through examining the results obtained by fitting to the WLF equation we have found that the WLF coefficient  $C_2$  is the same for both SHG and DR; on the other hand, we have found that the  $C_1$  coefficient is larger for dielectric relaxation. Finally, we have observed a lengthening of the SHG signal relaxation time in the bulk polymers subjected to successive poling/decay cycles that are similar to those observed in NLO chromophore polymer guest/host doped system. We have interpreted this phenomenon as being due to the gradual accumulation of trapped charges injected into the polymer matrix during the poling process.

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## Figure Captions

Figure 1: SHG rise and decay curves for a PI sample. The poling shown in Curve B was started approximately ten minutes after the SHG signal from shown in Curve A decayed to zero. Note the initial sharp and then gradual increase in SHG intensity in curve A and the almost immediate attainment of maximum SHG signal in curve B.

Figure 2: Two SHG decay curves for PI, the first curve obtained after the initial poling and the second one obtained after the steady state was reached. Note that the relaxation time of the second curve is an order of magnitude larger than that of the first.

Figure 3: Demonstration of the retardation effect in the SHG signal decay time. Here  $\tau_{ss}$  is the steady state average relaxation time and  $t_{elp}$  is the time from the end of the first poling duration. The solid line (slope = -0.3 corresponding to  $\gamma = +0.3$ ) was obtained by a linear fit to the entire data set according to the equation  $\tau = At_{elp}^{\gamma}$  discussed in the text.

Figure 4: Plot of SHG relaxation time versus  $1/T$  for (●) PI, (▼) PMMA and (▽) PVC. Solid lines represent fits to the VFT equation.

Figure 5: Comparison of (▽) dielectric and (▼) SHG relaxation times for PVC. Solid lines represent fits to VFT equation. Note that the SHG relaxation is much longer than the dielectric relaxation.

Table I

Selected KWW parameters obtained from curve fitting to Equation (1) and the calculated average relaxation times according to Equation (2) for those blank polymers studied.

	T /°C	$\tau$ /s	$\beta$	$\langle\tau\rangle$ /s
PI	207	2017	0.5216	3742
	215	321	0.480	692
	220	305	0.581	478
	225	211	0.621	304
	230	160	0.685	207
	235	148	0.686	191
PMMA	125	243	0.67	322
	130	96.9	0.74	117
	138	34.9	0.79	40.1
	141	24.8	0.68	32.5
	148	12.3	0.73	15.0
PVC	70.9	195.3	0.42	570.5
	75.5	194.8	0.589	436.2
	84.7	106.7	0.645	195.2
	90.3	55.8	0.692	89.468
	93.1	46.8	0.704	70.25
	103.4	31.3	0.865	33.7

## References and Notes

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immediately to its maximum value (c.f. Figure 1B); however, if some time had elapsed (i.e. one hour) then there was an initial fast growth followed by a slower segment (c.f. Figure 1A).

- <sup>15</sup> Results from the PVC and PMMA experiments show that the plateau SHG signal intensity remains fairly constant during successive poling/decay cycles. For PI the plateau SHG signal seems to fluctuate slightly and indeed returned to a higher value during the poling duration following that shown in 1B. This fluctuation in plateau intensity between the polings is not completely understood but its behaviour leads us to believe that the intensity decrease shown is not due to chemical degradation.
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